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Competing interests

The author declares no competing interests.



CLUSTER ANIONS

Stabilized resonances are no less exciting

Excited anion states provide doorways for molecular electron capture. Now, two-dimensional photoelectron spectroscopy of cluster anions has been shown to be a powerful tool for revealing the role of the local environment in facilitating the process.

C. Annie Hart and Richard Mabbs

Electron transfer is the most fundamental chemical process and considerable effort has been expended studying the interactions of low-energy electrons with neutral species. These electrons can be captured temporarily to form metastable anion states — or ‘resonances’ — that may result in energy transfer to or from the molecule or even dissociative electron attachment.

There are numerous important processes that involve dissociative attachment, such as the damaging of DNA through ionizing radiation^{1,2}, plasma remediation of air pollutants³, and ion chemistry in

the interstellar media⁴, to name but a few. Although these examples are diverse, they are linked by anion resonances acting as doorway states to electron capture. These resonances tend to be short-lived, sometimes on the order of picoseconds, but typically much shorter. Consequently, there is a lack of detailed experimental data to benchmark the sophisticated computational approaches required to deal with such non-stationary states. However, in a very promising development in this direction, Jan Verlet and colleagues now describe — in *Nature Chemistry* — the use of two-dimensional photoelectron

spectroscopy (2D-PES) to study sequentially solvated negative ions⁵. Using three selected parent anions ($C_{14}H_{10}^-$, $C_{13}H_9N^-$, $C_{13}H_8N_2^-$) and water-solvated variants ($C_{14}H_{10}^-(H_2O)_n$, $C_{13}H_9N^-(H_2O)_n$, $C_{13}H_8N_2^-(H_2O)_n$), they clearly demonstrate the effect that increasing solvation levels has on the resonances associated with these systems⁵.

The basic premise of 2D-PES is relatively straightforward. Photons remove electrons from negative ions and these photoelectrons are recorded as a function of their kinetic energy, producing a photoelectron spectrum. A series of such spectra are recorded at different photon energies and

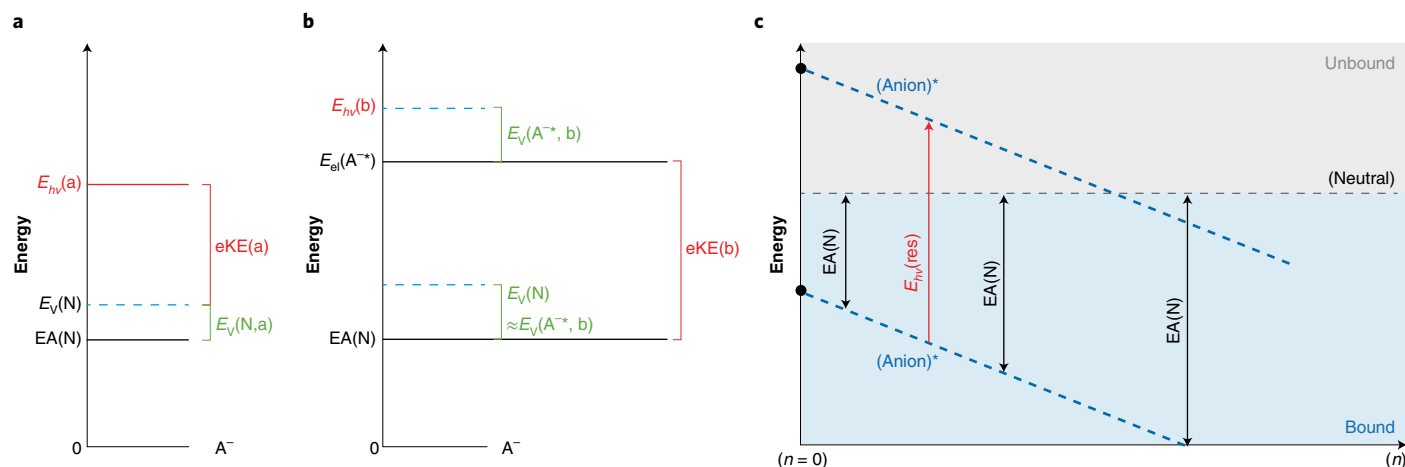


Fig. 1 | Schematic illustrating the states involved in anion photoelectron spectroscopy. a, Direct detachment at photon energy $E_{hv}(a)$. EA(N) is the electron affinity of the neutral and $E_v(N)$ is the vibrational energy of the neutral. **b**, Indirect detachment, $E_{hv}(b)$ excites a vibrational level of the anion excited state (A^*). **c**, As the number of water molecules is increased, the anion ground and excited states become more stable, and ultimately the excited state becomes bound (its energy is lower than that of the neutral ground state). However, the photon energy required to excite to the resonance ($E_{hv}(res)$) remains approximately the same.

collated (as a contour plot). The power of the approach is the ease of correlating the supplied photon energy to the probability of obtaining a particular outgoing electron kinetic energy. The kinetic energy distribution can be assigned to the structure of the neutral molecule left behind, however, 2D-PES acts as much more than a probe of the final, neutral structure, and immediately reveals 'direct' and 'indirect' electron loss processes.

'Direct' electron loss refers to electrons lost directly to the continuum. The kinetic energy of the electrons is determined as illustrated in the schematic of Fig. 1a. Assuming detachment takes place from the zero-point level of the anion (and ignoring rotation), $EA(N)$ and $E_V(N)$ are the electron affinity and the vibrational energy of the neutral, respectively. The range of $E_V(N)$ accessed is relatively independent of the supplied photon energy. On the other hand, 'indirect' means electron loss subsequent to excitation of a vibrational level of an anion resonance (A^*). This decays through electronic autodetachment, producing the neutral ground state and ejecting the excess electron. The vibrational energy from the resonance is (more or less) preserved throughout the autodetachment and the electron kinetic energy observed subsequent to excitation of different vibrational levels of the resonance is relatively constant. In Fig. 1b this is seen as $eKE(b) = E_{el}(A^*) - EA(N)$, where $E_{el}(A^*)$ is the electronic energy associated with the resonance.

Verlet and colleagues measured the 2D photoelectron spectra of $C_{14}H_{10}^-$, $C_{13}H_9N^-$, $C_{13}H_8N_2^-$ and several resonances were evident. They also measured the spectra of the solvated anions and revealed changes in the energies of the resonances and differences in the decay pathways. In particular, an increasing level of solvation is shown to promote internal conversion, both between different excited anion states and between these and high (ro) vibrational levels of the ground anion state through stabilization of the resonance. The increased lifetime enables internal conversion to compete with electron loss from the excited state.

Although using 2D-PES to study anions probes similar states to scattering experiments, the data obtained is complementary, rather than the same. Working on inherently charged species enables experimentalists to choose the level of solvation through mass spectrometric selection, and the response of the anion states to solvation can therefore be revealed.

Electron affinities are easily obtained and clearly increase as the number of water molecules increases⁵. This is a common observation in cluster anions, the solvent molecules reduce the energy of the anion ground state (relative to that of the neutral), as shown in Fig. 1c. In addition, $C_{14}H_{10}^-$, $C_{13}H_9N^-$, $C_{13}H_8N_2^-$ all exhibit evidence of low-lying resonances that are also observed in the monosolvated ($n = 1$) cluster anions. Similar to the ground anion state, 2D-PES also reveals stabilization of the resonance (Fig. 1c) in the presence of the water molecule. When the level of solvation is high enough the resonance is sufficiently stabilized to allow internal conversion to high (ro) vibrational levels of the ground anion state before electron loss. The spectra also clearly demonstrate the stabilization of a higher energy resonance in the $C_{14}H_{10}^-(H_2O)_n$ system, which produces electrons with progressively lower kinetic energy as n increases from 0 to 4. Most strikingly, the 2D spectra of the sequentially solvated cluster anions clearly show that, although solvation stabilizes the doorway states to electron capture (reducing energy, increasing lifetime), it has little influence on the relative energies of the ground and excited anion states. Gas-phase scattering experiments cannot yield this information because they do not probe electronically bound anion states – this would require a negative incident electron kinetic energy (eKE).

The marriage of cluster anion generation and 2D-PES is clearly an exciting development in the study of excited anionic systems. Changing the solvent molecule should be an obvious thing to do, however, there are several other exciting possibilities that 2D-PES of anions affords. Photoelectron spectroscopy has always been a relatively low resolution technique, but in 2D-PES this only refers to one domain, the eKE. The resolution in the photon energy domain is governed by the linewidth of the exciting radiation and in principle can be much higher. Contained within the 2D spectra will be action spectra for electron loss at a particular kinetic energy; therefore, 2D-PES probes the internal energy levels of any intermediate state that is accessed in the process. For example, much earlier work has revealed the rotational structure of a temporary excited anion state in the cyanomethide anion^{6,7}. Similar structure will be present in 2D spectra recorded in sufficiently small photon energy increments in the vicinity of a resonance. Such direct probing provides valuable benchmarks for theoretical treatments. To push the theme

of resolution a little further, in systems with better resolved vibrational structure in the electron kinetic energy domain, 2D-PES should reveal couplings between different vibrational channels⁸.

The ability to perform such experiments relies on efficient collection of photoelectrons with the ability to simultaneously measure their kinetic energies. 2D-PES is really only practicable because of the implementation of charged-particle imaging techniques such as velocity map imaging⁹. Images must be accumulated over tens of thousands of photon pulses before post-processing to create a 1D spectrum at a particular photon energy. The experiment is then repeated over many different photon energies to build the 2D spectrum. One can easily see why experiments measuring overall detachment cross-sections did not evolve into 2D spectra. Such an extension would have been prohibitively expensive in terms of time, effort and productivity. We strongly suspect that this 'scientific memory' is the reason why 2D-PES has lagged so far behind the implementation of the velocity map imaging technique⁹. Again, it must be stressed that these experiments are not quick and the work of Verlet and colleagues⁵ is an impressive effort. Nevertheless, as their results show, the information gained through 2D-PES of anions leads to significant new insights and offers a powerful technique, particularly for the probing of excited anion states. □

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Competing interests

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